Supporting Information

The effect of kaolinite on ferrihydrite colloids migration in soil: Molecular-scale mechanism study

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Section S1: Column dissection experiment

Retention profile of ferrihydrite colloids in the column was measured after the completion of each transport experiment, according to the procedures of Liao et al. 2020.¹ Specifically, each column was dismantled and dissected into 10 sections (~1 cm long each) to collect sands or kaolinite-coated sands (KL-sands) under gravity. 1 g sands or KL-sands of each section were put into 10 mL screw cap vials, then 6 mL of 1 M HNO₃ solution was added to each vial, all vials were shaken at 150 rpm for 12 h or longer to ensure the complete dissolution Fe(III). Concentrations of total Fe were measured using atomic absorption spectrometer (PinAAcle 900T, PerkinElmer).

Section S2: Isothermal titration calorimetry and Fe K-edge XAFS spectroscopy

The heat effect of the reaction between ferrihydrite colloids and KLs was measured by a thermal active monitor III (TAM III) system (Thermometric AB, Sweden). 0.7 mL of the adsorbent (KL, 20 g L⁻¹, pH 5.5) was added in a 1 mL stainless steel ampoule, and stirred with a gold propeller (120 r/min). Then automatic titration with ferrihydrite colloids (1 g/L, pH 5.5) in the syringe (Hamilton) (1 g/L) was performed, the volume of each titration was set as 10 μ L, the number of titrations was set as 20, and the interval of titrations was set as 600 s. The heat of dilute release was determined by titrating 5 mM NaNO₃ (pH 5.5) with ferrihydrite colloids. Data processing was conducted by the program NanoAnalyze software (version 3.7.5).

The X-ray absorption fine structure (XAFS) of the samples at the Fe K-edge were recorded on the beamline 44A at the Taiwan Photon Source synchrotron facility. Fe foil was used to calibrate the monochromator. The complexes sample of ferrihydrite adsorbed on kaolinite was examined in fluorescence mode. The Athena (version 0.9.26) was applied to pretreat the raw XAFS datas.² The k³ weighting function of the extended X-ray absorption fine structure (EXAFS) datas were then transformed to R-space by the fourier transformed fitting.^{2,3} The four parameters included Coordination number (N), bond length (R), Debye-Waller factor (σ 2) and E0 shift (Δ E₀) were obtained through the fitting of EXAFS spectra at Artemis program. The phase and amplitude

functions of the chosen scattering paths were obtained by the FEFF model.⁴

Section S3: The structure modeling and the calculations of adsorption energy

Previouse studies are general agreement that the iron is 75–100% octahedrally coordinated in the ferrihydrite structure.^{5,6} Therefore, model clusters of ferrihydrite were based on a dimer of two Fe³⁺ octahedron connected through two Fe–(OH)–Fe linkages as is believed to occur in ferrihydrite.⁷ KL is a dioctahedral 1:1 type phyllosilicate clay mineral with unit cell $Al_4Si_4O_{10}(OH)_8$.⁸ Each layer consists of a Si tetrahedral sheet and a Al octahedral sheet bound to each other by inner vertex oxygen centers, and these two-sheet layers are connected through hydrogen bonds.⁹

In the present study, the (010) facet of KL was chosen as an exemplary edge surface. Assuming that all suspended bonds are hydroxylated, the Al and Si centers maintain their coordination numbers. The models of KL and ferrihydrite was optimized using the Castep module of Material Studio 2020 (the specific methods in detail were described in materials and methods of the text). The stabilized initial structure of the KL and ferrihydrite were first calculated and presented in Figure S11. Three types of hydroxyl groups ('lying' (O₁H), 'upright' (O_uH), and 'tilted' (O_tH)) were observed on the Al-OH surface. These hydroxyl groups were energetically favorable for H-bond network, which was significantly influence the adsorption mechanism.¹⁰

The ferrihydrite adsorption energies were calculated by considering the reaction products. For example, the adsorption reaction in the Al octahedral sheet is

KL (Al) + ferrihydrite \rightarrow (KL (Al) - ferrihydrite) + nH₂O +mH₂ (S1)

The adsorption energy (E_{ads}) of ferrihydrite at the Al octahedral sheet of KL was described as

$$E_{ads} = (E_{\text{KL(Al)-f}} + nE_{H_2O} + mE_{H_2}) - (E_{\text{KL(Al)}} + E_f)$$
(S2)

where n and m were the number of the products of H_2O and H_2 , respectively. $E_{KL(Al)}$ was the total energy of KL specific facet, E_f was the total energy of ferrihydrite, and $E_{KL(Al)-f}$ was the total energy of the KL with adsorbing ferrihydrite. The total energies of isolated species (water, and H_2) were selected as the reference energies, which were calculated using DFT by the same methods with models of KL and ferrihydrite.

Section S4: Potential for transport of ferrihydrite colloids in porous media

To evaluate the effect of KL on the transport of ferrihydrite colloids, the maximum transport distance (L_{max}), which is defined as the distance that 99.9% of the particles retained in the medium, was determined based on the colloid filtration theory:¹¹

$$L_{max} = -\frac{2}{3(1-\theta)\alpha\eta_0} ln^{[i0]}(M_{eff})$$
(S3)

where d_c is the diameters of collector (2.5 cm), θ is the porosity of column (0.446), α is the attachment efficiency (i.e., number of ferrihydrite colloids that are retained on the sand or KL-sand collector divided by the number of ferrihydrite colloids that strike the sand or KL-sand collector), η_0 is the single-collector contact efficiency (i.e., number of ferrihydrite colloids that strike the sand or KL-sand collector), and M_{eff} is the single-collector divided by the number of ferrihydrite colloids that strike the sand or KL-sand collector), and M_{eff} is the effluent mass recovery of ferrihydrite colloids in the column experiments.

 α can be calculated by the following equation

$$\alpha = -\frac{2}{3(1-\theta)L\eta_0} ln^{[in]}(M_{eff})$$
(S4)

where L is the length of packed column (10 cm).

The deposition rate coefficient $\binom{k_d}{k_d}$ can be calculated using the below equation

$$k_d = \frac{3(1-\theta)}{2 \, d_c \theta} U \alpha \eta_0 \tag{S5}$$

where U is the fluid approach velocity (1 mL min⁻¹).

It's note that in a given condition, the values of k_d and L_{max} were determinated independent of α and η_0 , because the overall contribution of α and η_0 were counterbalanced in equations S3, S4, and S5. According to equations S4 and S5, the k_d can be calculated using the equation

$$k_d = \frac{Uln(M_{eff})}{L\theta}$$
(S6)

Consequently, while the definite values of α and η_0 were not calculated, the calculated values of k_d and L_{max} were reliable.¹² Liao et al. recently evaluated the k_d and L_{max} values of Cr(III)-HA-Fe(III) colloids used the similar calculated method.¹

The calculated values of k_d and L_{max} for the ferrihydrite colloids under conditions tested and the corresponding M_{eff} are tabulated in Table S2.

Section S5: Adsorption kinetic and isotherms

The ferrihydrite colloids adsorption processes were described by the pseudo-firstorder equation and the pseudo-second-order equation.

The pseudo-first-order equation ¹³

$$q_t = q_e(1 - \exp(-k_1 t))$$
 (S7)

where q_t and q_e (mg g⁻¹) are the amount of ferrihydrite colloids adsorbed at time t and equilibrium, k_1 (min⁻¹) is first order rate constant.

The pseudo-second-order equation 14

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{S8}$$

where k_2 (g mg⁻¹ min⁻¹) is the rate constant of pseudo-second-order.

The adsorption equilibrium was described by three two-parameter isotherm models (Langmuir, Freundlich, and Temkin) and two three-parameter adsorption isotherm models (Redlich–Peterson and Sips).

The Langmuir adsorption isotherm model assume that adsorption takes place at the specific homogeneous sites within adsorbent. The equation as follow ¹⁵

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{S9}$$

where q_m (mg g⁻¹) is the theoretical maximum monolayer adsorption capacity, K_L (L mg⁻¹) is the equilibrium constant, and C_e is the equilibrium concentration of ferrihydrite colloids (mg L⁻¹), q_e is the amount of ferrihydrite colloids adsorbed per unit quality of the KL at equilibrium (mg g⁻¹).

Basic assumption of Freundlich isotherm assumes is that adsorption takes place at heterogeneous surface with a nonuniform distribution of adsorption heat. The equation is given as ¹⁶

$$q_e = K_f C_e^{1/n} \tag{S10}$$

where K_f and 1/n are indicative parameters of adsorption capacity and intensity, respectively.

Temkin adsorption isotherm model assumes that the decrease adsorption heat is linear and the adsorption binding energies is uniform distribution. Temkin isotherm is expressed as.¹⁷

$$q_e = \frac{RT}{b} ln^{\text{mol}}(K_{Te}C_e) \tag{S11}$$

where R is the gas constant (8.314×10⁻³ kJ K⁻¹ mol⁻¹), T is the absolute temperature (K), b is related to the adsorption heat (J mol⁻¹), and K_{Te} is the equilibrium binding constant (L g⁻¹).

Redlich–Peterson adsorption isotherm model proposed an empirical equation to represent the equilibrium data. The model is written as ¹⁸

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \tag{S12}$$

where K_R (L g⁻¹) and a_R (L mg⁻¹) are the isotherm constants, and β is the exponent that lies between 0 and 1. This equation reduces to a Langmuir isotherm when $\beta=1$.

Sips adsorption isotherm model like the Freundlich isotherm at low sorbate concentrations, while approximates to the Langmuir isotherm at high concentrations.¹⁹ It is expressed as ²⁰

$$q_{e} = \frac{q_{m}a_{s}C_{e}^{1/n}}{1 + a_{s}C_{e}^{1/n}}$$
(S13)

where a_s is the Sips constant that related to adsorption energy.



Figure S1. The standard curve of ferrihydrite colloids at an absorbance of 420 nm.



Figure S2. XRD patterns of as-prepared ferrihydrite colloids.



Figure S3. HRTEM images of as-prepared ferrihydrite colloids (a). Histograms of the particle distribution of ferrihydrite colloids, which measured statistically from a number of different regions images (b).



Figure S4. The average hydrodynamic diameter of ferrihydrite colloids as a function of pH.



Figure S5. The SEM micrographs of (a) clean quartz sand, (b) KL-sand and (c) pure KL. (d) The SEM-EDS spectra of the red dot of (a) and (b).



Figure S6. Desorption of ferrihydrite colloids from KL at different pH (a), different concentrations of NaNO₃ (b) and citrate (c). The concentrations of free Fe^{3+} as a function of time in desorption solution by citrate (d).



Figure S7. The SEM-EDS spectra of the KL and KL-ferrihydrite colloids (a). The TEM-EDS spectra of KL-ferrihydrite colloids complexes (the area 1 and 2 in Figure 3f) (b).



Figure S8. TEM images of ferrihydrite absorbed on KL (a), and the corresponding HAADF-STEM images (b) and EDS mappings of O (c), Si (d), Al (e) and Fe (f).



Figure S9. Fe K-edge EXAFS spectra (blank dots) and its model fits (colored lines) of ferrihydrite (a), KL-ferrihydrite for Al/Si as the backscat-tering atom (b), and KL-ferrihydrite for Fe as the backscat-tering atom(c). The peak locations correspond to interatomic distances and are uncorrected for phase shifts. The EXAFS spectra of ferrihydrite (d), KL-ferrihydrite for Al/Si as the backscat-tering atom (e), and KL-ferrihydrite for Fe as the backscat-tering atom (f) weighted by K³.



Figure S10. Optimized bulk and surface structure of ferrihydrite and KL. (a) two Fe³⁺ octahedron represent ferrihydrite; (b) the (010) facet of KL. The red, purple, pink, cyan and white spheres represent oxygen, iron, aluminum, silicon and hydrogen atoms, respectively.

pH NaNO ₃ (mM)			Sand		KL-sand		
		Meff (%)	$k_{d\ (10^{-5}{ m s}^{-1})}$	Lmax (m)	Meff (%)	$k_{d(10^{-5} \text{ s}^{-1})}$	Lmax (m)
5.5	5	90.8±0.14	7.33±0.12	7.19±0.11	64.1±0.13	34.0±0.16	1.55±0.07
5	5	92.3±0.30	6.10±0.25	8.65±0.35	68.2±0.24	29.1±0.27	1.81 ± 0.02
4	5	95.2±0.01	3.78±0.01	13.9±0.04	72.7±0.30	24.3±0.32	2.16±0.03
3	5	96.9±0.16	2.39±0.12	22.1±1.17	73.8±0.29	23.2±0.30	2.27±0.03
5.5	1	93.4±0.19	5.21±0.15	10.1±0.29	75.8±0.02	21.2±0.02	2.49±0.01
5.5	5	90.8±0.14	7.33±0.12	7.19±0.11	64.1±0.13	34.0±0.16	1.55 ± 0.07
5.5	10	89.6±0.10	$8.34{\pm}0.08$	6.31±0.06	58.9±0.06	40.3±0.08	1.31±0.03

 Table S1. Effect of KL on the Mass Percentages, Deposition Rate and Predicted Maximum

 Travel Distance of Ferrihydrite Colloids in Column Experiments.

Table S2. The Kinetics Parameters of Ferrihydrite Colloids Adsorption onto KL.

	Pseudo-first order			Pseudo-second order		
	$q_{e(mg g^{-1})}$	$k_{1(\min^{-1})}$	R ²	$q_{e(mg g^{-1})}$	$k_{2(g mg^{-1} min^{-1})}$	R ²
рН 5.5	19.0	1.73	0.9992	19.3	0.197	0.9999
pH 5.0	18.2	1.76	0.9992	18.5	0.219	0.9999
pH 4.0	16.2	1.69	0.9996	16.5	0.235	0.9999
pH 3.0	15.8	1.50	0.9989	16.0	0.195	0.9995
1 mM NaNO3	12.1	1.68	0.9969	12.4	0.220	0.9984
5 mM NaNO3	19.0	1.73	0.9992	19.3	0.197	0.9997
10 mM NaNO3	24.3	1.67	0.9994	24.7	0.151	0.9997

Table S3. The Isotherm Parameters of Ferrihydrite Colloids Adsorption onto KL.

Models				
Langmuir	<i>q_{m(mg g⁻¹)}</i> 19.6	$K_{L(L mg^{-1})}$ 3.51	R ² 0.991	
Freundlich	$K_{f(mg g^{-1})}$ 15.8	1/n 0.0793	R ² 0.841	
Temkin	<i>К_{Te}</i> (L g ⁻¹) 76569	b (J mol ⁻¹) 1.76	R ² 0.882	

Redlich-Peterson	$K_{R(L g^{-1})}$	$a_{R(L mg^{-1})}$	β	R ²
	81.1	4.3	0.985	0.998
	<i>a</i>			
Sips	$q_m(\text{mg g}^{-1})$	a_s	1/n	R ²
	20.2	3.21	0.737	0.999

Table S4. EXAFS Fitting Parameters at the Fe K–Edge for Various Samples ($S_0^2 = 0.72$).

Sample Shell		CNa	$R(\text{\AA})^b$	$\sigma^2(\text{\AA}^2)^c$	$\Delta E_0(\mathrm{eV})^d$	R factor
	Fe-O	5.4±0.4	1.95 ± 0.02	0.0092 ± 0.0013	7.1±1.0	
FNPs	Fe-Fe1	2.6±1.3	$3.02{\pm}0.01$	0.0061 ± 0.0026	9.5 ± 1.9	0.00143
	Fe-Fe2	3.1±1.4	3.24 ± 0.02	$0.0097 {\pm} 0.0039$	-5.3±1.8	
FNPs-KL	Fe-O	6.9±1.6	1.98 ± 0.01	0.0079 ± 0.0026	6.6±1.4	
	Fe-Al/Sil	2.5 ± 0.7	$3.02{\pm}0.01$	0.0074 ± 0.0024	$-8.0{\pm}1.8$	0.0103
	Fe-Al/Si2	3.9±1.0	3.28 ± 0.03	$0.0067 {\pm} 0.0038$	7.1±1.5	
	Fe-O	6.8 ± 1.7	$1.97{\pm}0.02$	0.0092 ± 0.0013	8.1±1.5	
FNPs-KL	Fe-Fe1	2.6 ± 0.8	3.04 ± 0.03	0.0061 ± 0.0026	9.2±2.4	0.0141
	Fe-Fe2	3.8±1.5	3.29 ± 0.02	$0.0097 {\pm} 0.0039$	-6.4±1.1	

^{*a*}*CN*, coordination number; ^{*b*}*R*, distance between absorber and backscatter atoms; ^{*c*} σ^2 , Debye-Waller factor to account for both thermal and structural disorders; ^{*d*} ΔE_0 , inner potential correction; *R* factor indicates the goodness of the fit. S₀² was fixed to 0.72, according to the experimental EXAFS fit of Fe foil by fixing CN as the known crystallographic value. A reasonable range of EXAFS fitting parameters: $0.700 < S_0^2 < 1.000$; *CN* > 0; $\sigma^2 > 0$ Å²; $|\Delta E_0| < 10$ eV; *R* factor < 0.02.

 Table S5. Reactions Considered for the Adsorption Energy Calculations and Corresponding

 Values Obtained for Ferrihydrite Adsorption on KL.

System	Energetic calculations	Eads (eV)
Al octahedral sheet		
MM	$(E_{KL(Al)-f}+0.5E_{H2}+E_{H2O})-(E_{KL(Al)}+E_{f})$	7.05
MB	$(E_{KL(Al)-f}+E_{H_2O})-(E_{KL(Al)}+E_f)$	-0.03
BM	$(E_{KL}(AI)-f+H_2+2E_{H_2O})-(E_{KAOLIN(AI)}+E_f)$	6.49
Si tetrahedral sheet		
MM	$(E_{KL(Si)-f}+0.5E_{H_2}+E_{H_2O})-(E_{KL(Si)}+E_f)$	-3.48
BM	$(E_{KL(Si)-f}+2E_{H_2O}+E_{H_2})-(E_{KL(Si)}+E_f)$	5.83
BB	$(E_{KL(Si)-f}+2E_{H_{2}O}+E_{H_{2}})-(E_{KL(Si)}+E_{f})$	5.31

MM, MB, BM and BB were denoted as monodentate mononuclear, monodentate binuclear, bidentate mononuclear, and bidentate binuclear.

System				
Al octahedral sheet	dates (Å)	dra o (Å)	dato (Å)	∠Al–O–Fe (°)
MM	3.36	1.69	1.98	132.64
MB	3.56/3.20	1.77	1.98/1.90	143.15/121.49
BM	3.10	1.73/1.91	1.80/3.14	122.83/70.98
Si tetrahedral sheet	d _{Si-Fe} (Å)	d _{Fe-O} (Å)	d _{Si-O} (Å)	∠Si–O–Fe (°)
MM	3.05	1.76	1.67	125.37
BM	2.55	1.79/1.81	1.64/1.65	95.81/74.74
BB	3.24/3.15	1.76/1.74	1.67/1.67	133.13/143.36

Table S6. Structural Parameters of Ferrihydrite Colloids Adsorption Configurations on KL.

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